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SUPPLEMENTAL REPORT ON

LABORATORY STUDY ON FEASIBILITY OF MUNITIONS  
WASTEWATER TREATMENT BY ADSORPTION-OXIDATION.

*Supplement*

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(11) 31 Jan 76

(12) 18p.

PREPARED FOR

U.S. ARMY MOBILITY EQUIPMENT

RESEARCH AND DEVELOPMENT CENTER

SANITARY SCIENCES DIVISION, FT. BELVOIR, VIRGINIA

(15) CONTRACT DAAG53-75-C-8273

JANUARY 31, 1976

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GENERAL ELECTRIC  
Re-entry & Environmental  
Systems Division

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## INTRODUCTION AND OBJECTIVE

✓ This report is a supplement to the main report on the Laboratory Study on feasibility of Munitions Wastewater Treatment by Adsorption-Oxidation, submitted for the contract #DAAG53-75-C-0273. Based on the results of the study, the existence of adsorption-oxidation effect was demonstrated using experimental data on the removal of TNT; and ~~furthermore~~ it was also concluded that a lack of reactivity of RDX and HMX towards ozone was seemingly responsible for the absence of the adsorption-oxidation effect in their cases. This supplemental report presents the results of a preliminary investigation on the effects of using an advanced adsorption-oxidation technique on munitions waste treatment. The technique is based on the concept of increasing the reactivity of an organic material towards ozone by exposing the material to ultraviolet (UV) radiation during ozonation. Batch experiments were performed on solutions of TNT, RDX, and HMX to demonstrate the increased rate of reaction of an organic with ozone in the presence of ultraviolet radiation; continuous flow experiments were conducted to show the enhanced adsorption-oxidation effect with ultraviolet radiation and ozonation. ↗

## SCOPE

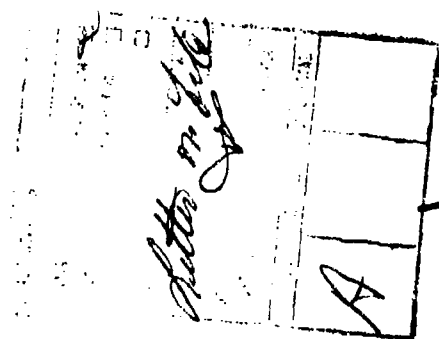
All experiments were conducted on solutions of organic materials in tap water at room temperature.

### Batch Experiments

- Ozonation of TNT, RDX, and HMX solutions with and without UV radiation

### Flow Experiments

- Adsorption-Oxidation of TNT and RDX solutions using ozone and UV radiation.
- Adsorption of TNT and RDX solutions (reference experiments without ozone or UV radiation).



In the flow experiments, conditions regarding the liquid overflowrate (gpm/ft<sup>2</sup>) and contact time of carbon with liquid were maintained almost identical to those for the previous experiments described in the main report. However the column design for experiments described in this report differed significantly from that in the main report; this was unavoidable since the scope of the two tasks were considerably different. The differences in the column design are discussed in the following section.

Experimental conditions in the flow experiments are summarized below:

TNT	~ 20 mg/l; ~ 35 mg/l
RDX	~ 10 mg/l; ~ 20 mg/l
Concentration of Ozone in Feed Gas	~ 11.5 mg/l; ~ 23 mg/l
Liquid Flowrate	~ 20 ml/min
Gas Flowrate	175-205 cc/min

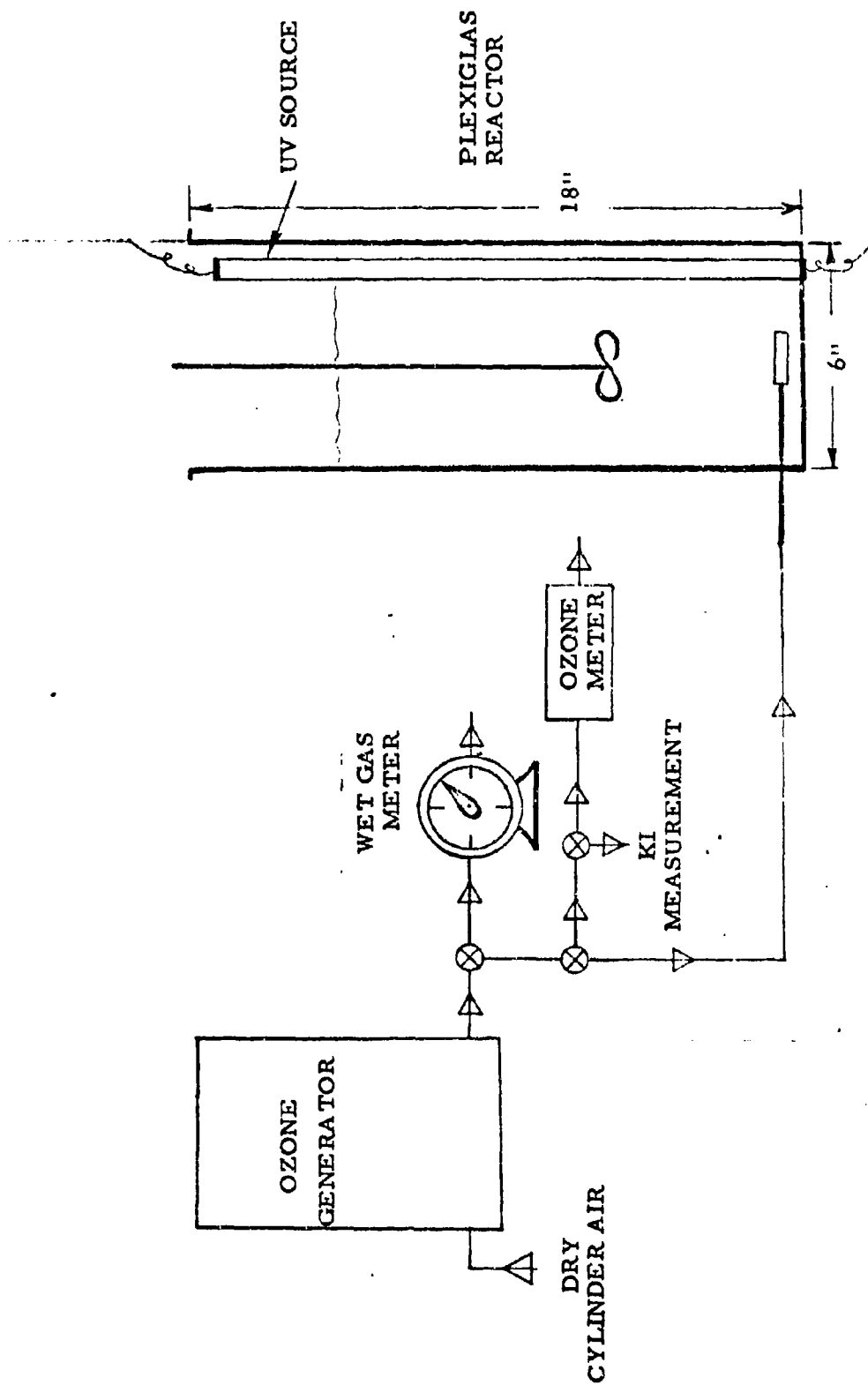
#### TEST SETUP

Batch Experiments: The test setup consisted of a plexiglas reactor fitted with a 15 watt germicidal lamp (G15T8, General Electric) for UV radiation as shown in Figure 21. Ozone gas was introduced at the bottom through a gas sparger and its concentration in the feed gas was measured using an in-line Ozone Meter (Source Gas Analyzer). The gas-liquid mixture was vigorously stirred using a high speed motor-stirrer to increase the contact of ozone with the dissolved organics.

Continuous Flow Experiments: The test setup as shown in Figure 22 was basically similar to that for the previous experiments described in the main report. Experiments were conducted using quartz columns instead of the plexiglas columns; the adsorption-oxidation column was irradiated with UV light by two 15 watts germicidal lamps placed side by side adjacent to the column while the

FIGURE 21

TEST SETUP FOR BATCH EXPERIMENTS

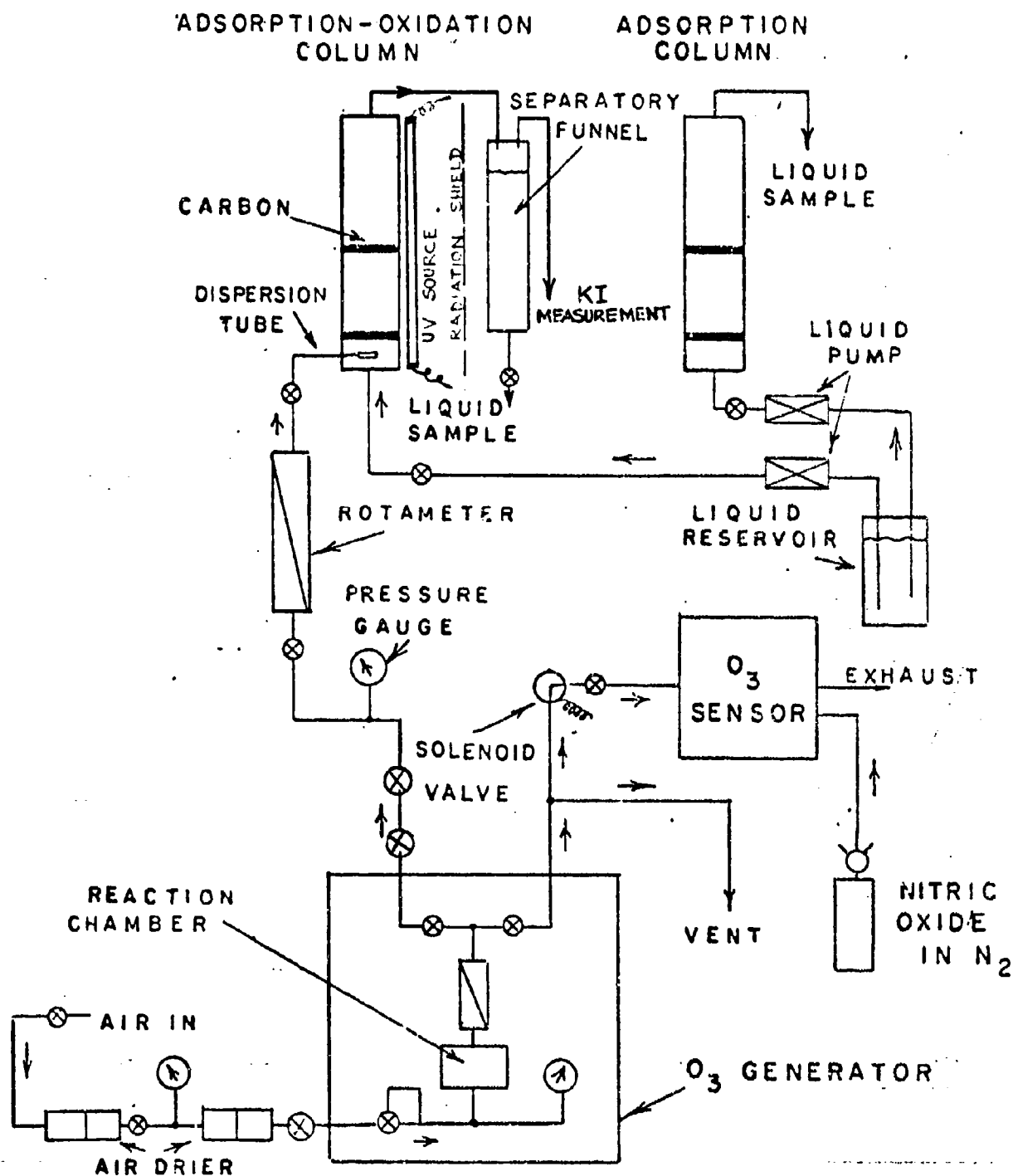


adsorption column was not exposed to UV radiation. The column design differed in three significant details from the plexiglas columns used previously: (i) ozone was introduced at only one point in the adsorption-oxidation column, at the bottom, instead of three; (ii) the quartz column was  $1 \frac{1}{16}$ " i.d. x 15" high compared to  $1 \frac{1}{8}$ " i.d. x 30" high plexiglas column (iii) only two carbon layers were packed in each column (2.9 grams of carbon/layer) instead of three in the plexiglas column (2.0 grams of carbon/layer), although the total amount of carbon packed in a quartz column (5.8 gms) was comparable to that in the previous experiments (6.0 gms.). These differences in the column design are likely to impact the adsorption-oxidation process significantly more than the adsorption process primarily because of differences in the method of gas-liquid contacting and the gas-liquid contact time. The influent gas measurements on ozone concentration were made using an inline Ozone Meter while the ozone in the effluent gas from the adsorption-oxidation column was measured using KI method.

## EXPERIMENTS

The methods for preparing the test solutions and for making analytical measurements on the treated and untreated samples are described in detail in the main report and will, therefore, not be repeated here.

Batch Experiments: A 5-litre batch of the test solution was charged into the plexiglas reactor and ozonated for a period of 2 hours. The gas-liquid mixture was vigorously stirred using a motor-driven stirrer throughout each run. For each experiment, two runs were made; one with the UV radiation and, the second without any radiation. Liquid samples were withdrawn periodically from the reactor and analyzed for specific organic chemical present in the solution. Ozone concentrations in the influent gas were measured on an in-



TEST SETUP—FLOW DIAGRAM

FIGURE 22

line Ozone Meter which was calibrated using KI method. The gas flowrate into the column was measured on a wet gas meter.

Flow Experiments: The experimental procedure is basically the same as described in the main report. Columns were packed for each run, and desired experimental conditions were set regarding the liquid flowrate, gas flowrate, feed concentration of organic material in solution, and ozone concentration in the feed gas. All these conditions were monitored and checked repeatedly during the course of a run to ensure that they stayed constant. Liquid samples were collected from each column periodically for analysis. Each run was carried out for approximately 6 hours.

## RESULTS AND DISCUSSION

The data on the batch experiments are presented in Figures 23-25 for TNT, RDX, and HMX respectively. In each case it is seen that with the introduction of UV, the rate of disappearance of an organic chemical upon ozonation increased dramatically.

The data on the flow experiments are given in Tables I and II for TNT and RDX respectively. Experimental conditions selected for a given run are also included in these tables. A comparison between the adsorption-oxidation and the adsorption processes for TNT solutions is illustrated in Figure 25, and for RDX in Figure 27. It can be seen that the adsorption-oxidation performs better than adsorption in both cases, more significantly for TNT than for RDX. A quantitative evaluation of the effect of UV radiation on adsorption-oxidation can not be made since the column designs in the two series of experiments are quite different; however a qualitative assessment of the improvement due to UV can be made by comparing the TNT data in Figure 26 with that in Figure 10 (main report) and by comparing the RDX data in Figure 27 with that in Figure 11 (main report). The comparison shows that the adsorption-oxidation effect is somewhat enhanced for both TNT and RDX by combining UV with ozonation.

FIGURE 23

OZONATION OF TNT WITH AND WITHOUT UV

INITIAL TNT CONC. = 35 mg/l

VOLUME OF TNT SOLUTION = 5 litres

GAS FLOWRATE = 160 cc/min

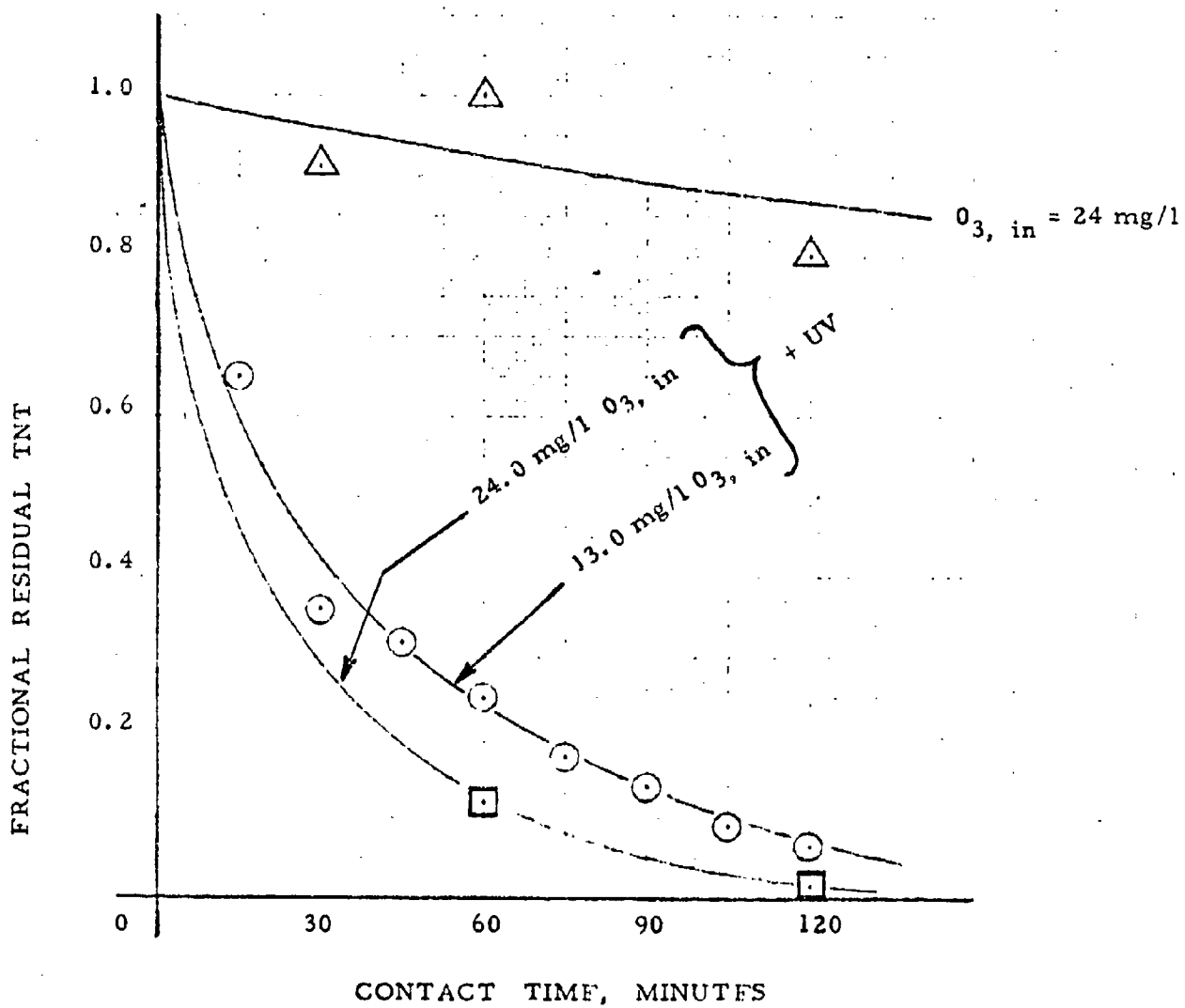


FIGURE 24

OZONATION OF RDX WITH AND WITHOUT UV

INITIAL RDX CONCENTRATION = 24.6 mg/l

VOLUME OF RDX SOLUTION = 5 litres

GAS FLOWRATE = 160 cc/min

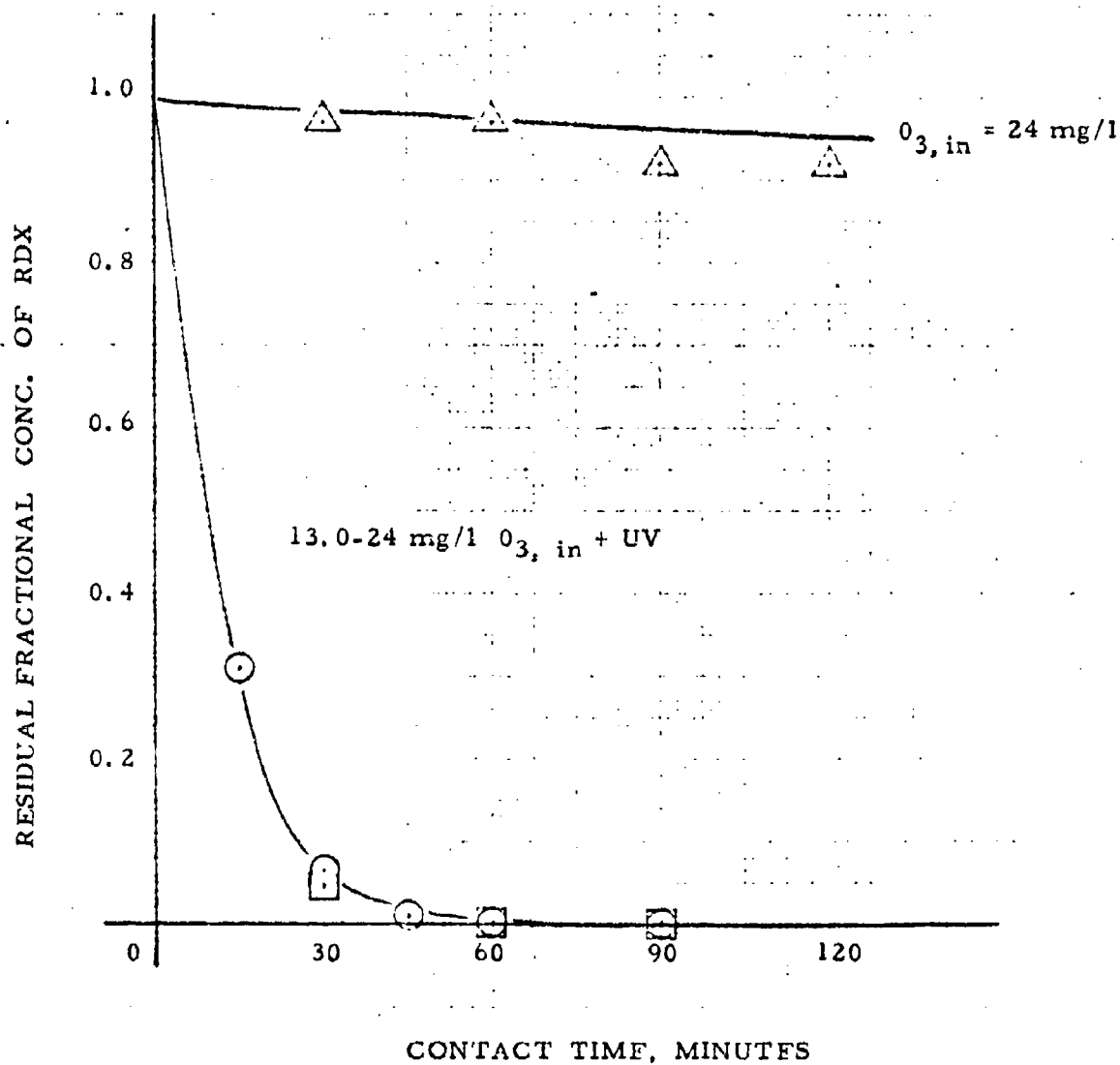


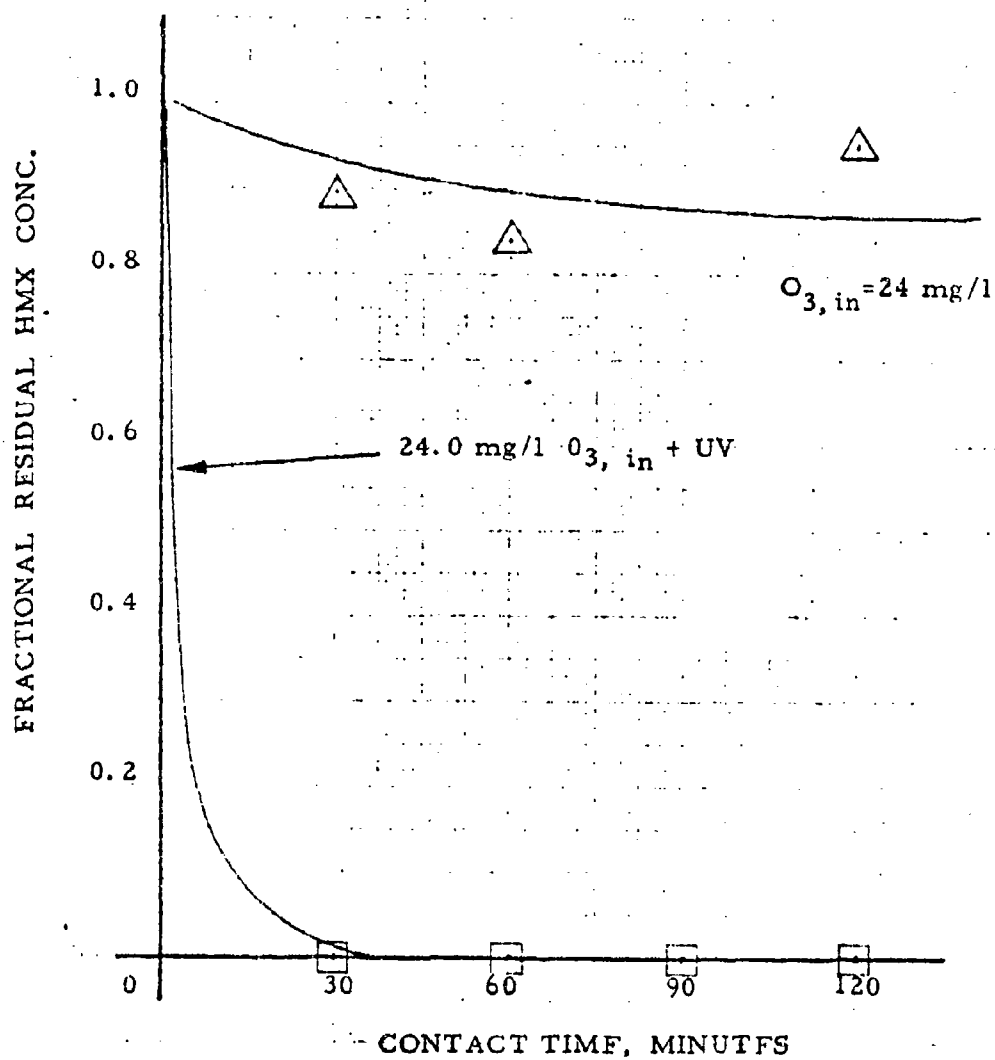
FIGURE 25

OZONATION OF HMX WITH AND WITHOUT UV

INITIAL HMX CONC. = 4.24 mg/l

VOLUME OF HMX SOLUTION = 5 litres

GAS FLOWRATE = 160 cc/min.



The adsorption characteristics for respective chemicals in the two series of experiments are almost identical which means that the differences in the adsorption column design in the two series are not significant. This is not unexpected since the operating conditions such as liquid over flowrate (gpm/ft<sup>2</sup>), total carbon-liquid contact time, and feed concentration of the organic chemical were kept the same in the two series. Furthermore, this agreement on the adsorption data between the two series of experiments also confirms the reproducibility of the data.

As described earlier, the introduction of UV does seem to enhance the adsorption-oxidation effect for both TNT and RDX, however the enhancement is not equivalent to the increase in reactivity demonstrated by the batch data. Evidently there are significant differences in the two experiment designs which are believed to be primarily responsible for such a significant difference in behavior. The gas-liquid contact in the batch experiments is very thorough due to high speed stirring and a lot of gas-liquid interfacial surface is created due to high shear rate. Such conditions do not exist in the flow experiments as designed in this study since ozone is introduced at a single point only; consequently mass transfer of ozone is not as efficient. Furthermore the power input due to UV per unit volume of liquid is certainly much higher in the batch experiments than in the flow experiments. In the batch experiments, the UV surface was surrounded by liquid on all sides whereas in the flow reactor, the UV source was located outside adjacent to the column and due to curvatures of the column and the UV source, only a small fraction, ~15-25%, of the column surface was directly exposed to the UV source. A direct exposure of the reaction mixture to UV is important since transmittance of UV attenuates very rapidly in a liquid limiting the active reaction ozone to a thin film. The thickness of the active reaction zone due to UV is profoundly affected by the presence

FIGURE 26

ADSORPTION-OXIDATION AND ADSORPTION OF TNT

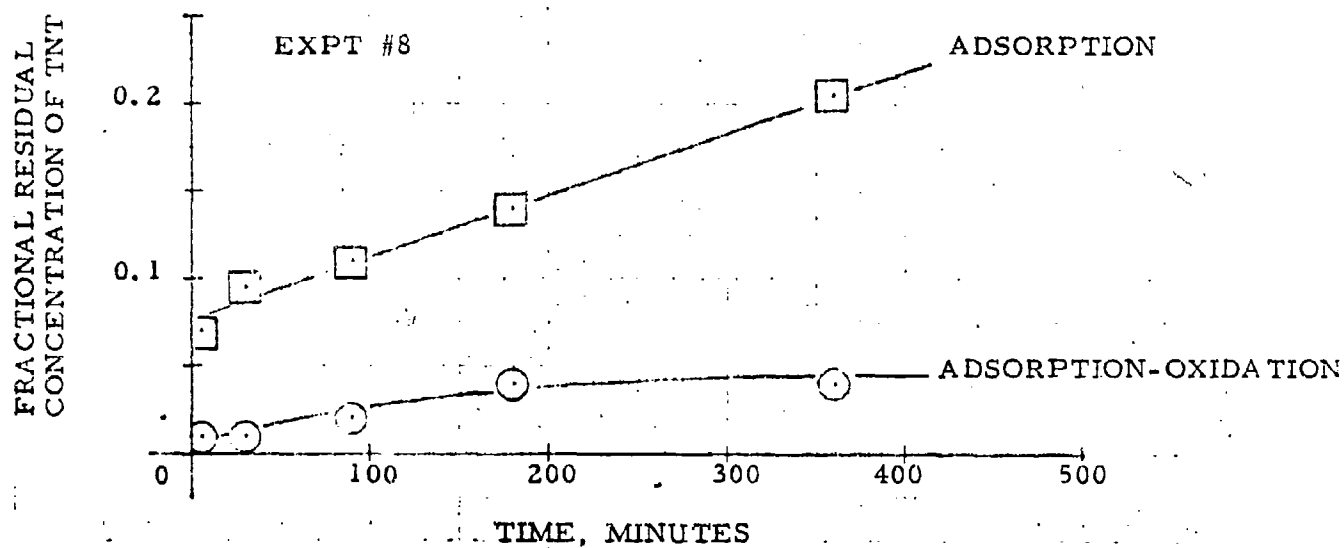
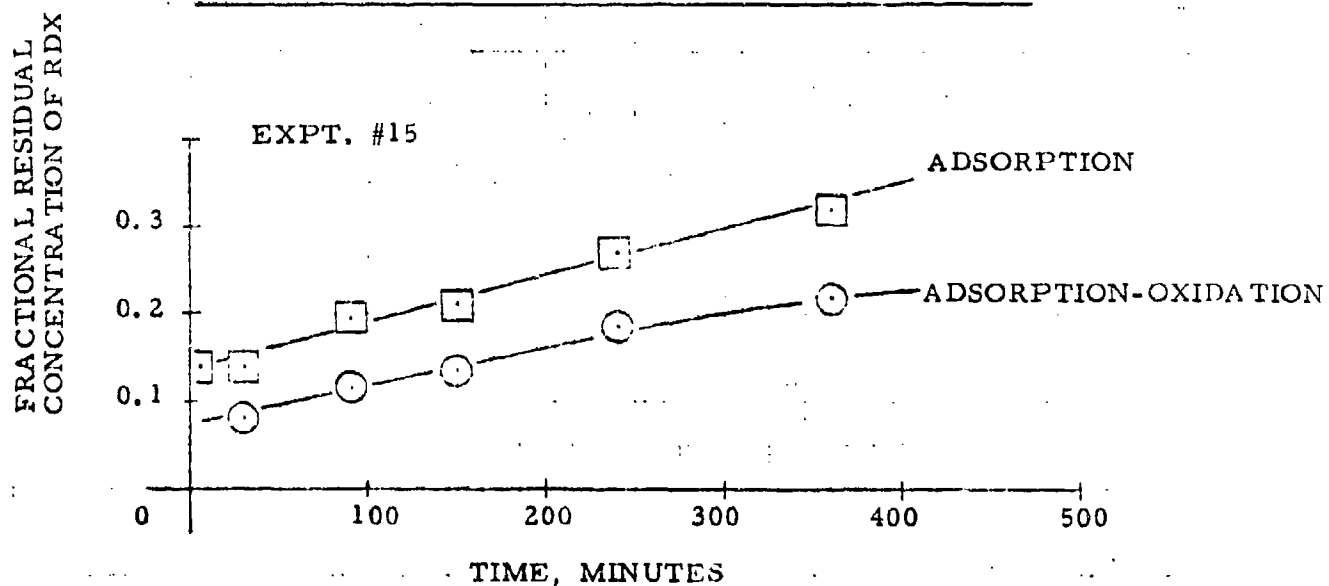


FIGURE 27

ADSORPTION-OXIDATION AND ADSORPTION OF RDX



of dissolved solids or of organic matter (L. R. Koller, "Ultraviolet Radiation", John Wiley & Sons, Inc., Second Edition, 1965, page 186). For example the adsorption coefficient at  $2537 \text{ \AA}$  of the drinking water for nineteen large United States cities varied by a factor of 7 (M. Luckiesh, Gen. Elec. Rev., 47, 1944, page 26). Due to high speed stirring in the batch experiments, a fresh liquid surface was rapidly and continuously being exposed to UV radiation. Such conditions obviously did not exist in the flow experiments. A comparison of the conditions for batch vs. flow experiments is illustrated in Figure 28 and it clearly shows that in the flow experiments, only a very small portion of the total flow benefitted from the UV exposure whereas in the batch experiments, total liquid volume was exposed to UV due to high speed mixing. Based on the batch data, it also seems reasonable to assume that the reactions of all three test chemicals, TNT, RDX and HMX, occur very rapidly with ozone in the presence of UV under favorable reaction conditions.

The limitations of the design of the test setup for flow experiments described in this supplemental report were understood before the experiments were conducted; however considerations of limited resources and time required the test setup design to be the simplest and the most inexpensive possible. It can be seen however that the objectives of the task have been fulfilled even with such a simple test setup.

These results also clearly show a need for developing a better method of gas-liquid contact and also for bringing the gas-liquid mixture into a direct exposure of the UV radiation in the flow experiments. One method of improving the gas-liquid contact is by multipoint introduction of ozone as designed for the previous series of experiments described in the main report. As pointed out in the main report, multipoint introduction of ozone is also important for minimizing loss of ozone due to auto-decomposition reaction.

Further modifications of that design will be required to improve the method of exposing the gas-liquid reaction mixture to UV radiation.

#### CONCLUSIONS AND RECOMMENDATIONS

- The adsorption-oxidation effect can be enhanced by increasing the reactivity of the organic material towards ozone.
- The reactivity of the chemicals TNT, RDX, and HMX towards ozone is increased dramatically by exposing the liquid to ultraviolet radiation during ozonation.
- For achieving high rates of reaction, it is necessary to create hydraulic conditions of complete mixing between the gas and the liquid, and also conditions of intimate contact between the surface of the UV source and the gas-liquid mixture. The flow-through experiment design used for experiments described in this supplemental needs to be modified to provide for both conditions.
- The study should be expanded to study the effects of the composition of the feed solution using advanced adsorption-oxidation method. The importance of this variable has already been demonstrated based on the data presented in the main report.
- As pointed out in the main report, a comprehensive data base needs to be generated to obtain necessary information for designing a treatment system for actual munitions waste. Several key areas have been identified for further work; these include carbon life data, quantitative measures on the effects of the chemical characteristics and composition of actual munitions waste, quantitative evaluation of the process variables in the advanced adsorption-oxidation method, and optimization of the process with respect to the engineering parameters such as contact time of the liquid with gases and carbon, feed concentration of ozone, number of carbon layers, carbon layer thickness, flowrates of liquid and gas, mode of gas liquid contact, UV power input per unit volume of liquid, and design for creating close contact of the UV source surface with liquid.

FIGURE 28

BATCH VS. FLOW REACTOR CONDITIONS

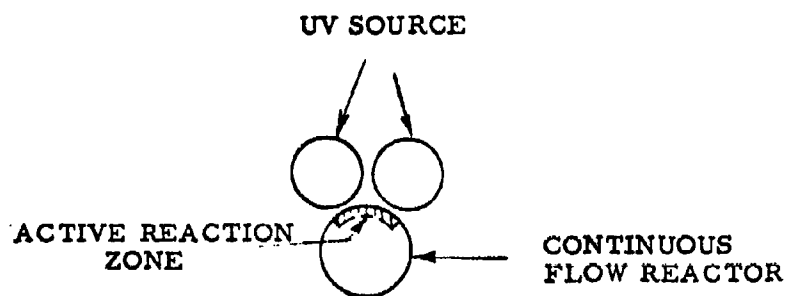
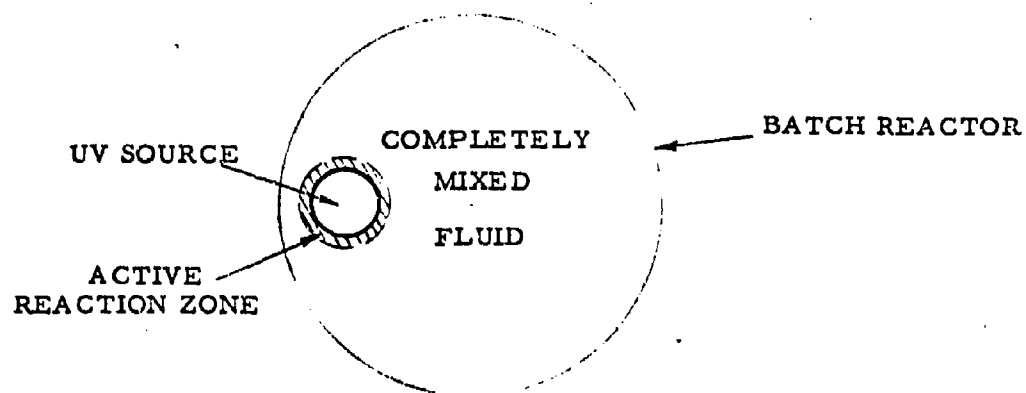


TABLE I  
EXPERIMENTAL DATA ON REMOVAL OF TNT

		EXPERIMENT #7		EXPERIMENT #8		
		A/O Column	Ads. Column	A/O Column	Ads. Column	
Initial Conc. of TNT, mg/l =		20.0	20.0	20.0	20.0	
Liquid Flowrate , cc/min =		20.0	20.0	20.0	20.0	
Gas Flowrate , cc/min =		205	--	200	--	
O <sub>3</sub> Conc. in Feed Gas, mg/l =		11.2	--	21.5	--	
O <sub>3</sub> Conc. in Exit Gas, mg/l =		7.1	--	16.0	--	
Sample Time, min		$\frac{C_1}{C_0}$	$\frac{C_2}{C_0}$	Sample Time, min	$\frac{C_1}{C_0}$	$\frac{C_2}{C_0}$
5		0.007	0.075	5	0.01	0.07
30		0.015	0.095	30	0.01	0.095
60		--	--	90	0.02	0.11
120		0.04	0.14			
180		0.05	0.16	180	0.04	0.14
240		--	--	240	--	--
360		0.065	0.205	360	0.04	0.205

TABLE I (CONT'D)  
EXPERIMENTAL DATA ON REMOVAL OF TNT

		EXPERIMENT #9		EXPERIMENT #10			
		A/O Column	Ads. Column		Ads. Column	Ads. Column	
Initial Conc. of TNT, mg/l =		35.2	35.2		33.7	33.7	
Liquid Flowrate , cc/min =		22.0	22.0		20.0	20.0	
Gas Flowrate , cc/min =		185	--		188	--	
O <sub>3</sub> Conc. in Feed Gas, mg/l =		23.3	--		12.35	--	
O <sub>3</sub> Conc. in Exit Gas, mg/l =		13.66	--		7.97	--	
		Sample Time, min.	$\frac{C_1}{C_0}$	$\frac{C_2}{C_0}$	Sample Time, min.	$\frac{C_1}{C_0}$	$\frac{C_2}{C_0}$
		5	0.054	0.12	5	0.02	0.10
		30	--	--	30	0.047	0.14
		60	0.065	0.14	60	--	--
		120	0.074	--	120	0.059	0.16
		180	--	--	180	0.089	0.23
		240	0.11	0.22	240	0.107	0.29

TABLE II  
EXPERIMENTAL DATA ON THE REMOVAL OF RDX

		EXPERIMENT #15		EXPERIMENT #16			
		A/O Column	Ads. Column	A/O Column		Ads. Column	
Initial Conc. of RDX, mg/l =		18.0	18.0	9.9		9.9	
Liquid Flowrate , cc/min =		20.0	20.0	20.0		20.0	
Gas Flowrate , cc/min =		185	--	175		--	
O <sub>3</sub> Conc. in Feed Gas, mg/l =		20.85	--				
O <sub>3</sub> Conc. in Exit Gas, mg/l =		19.0	--				
		Sample Time, min.	$\frac{C_1}{C_0}$	$\frac{C_2}{C_0}$	Sample Time, min.	$\frac{C_1}{C_0}$	$\frac{C_2}{C_0}$
		5	--	0.14	5	--	0.08
		30	0.08	0.14	30	--	--
		90	0.116	0.194	90	0.09	0.12
		150	0.138	0.211	150	0.11	0.15
		240	0.188	0.27	240	0.15	--
		360	0.22	0.32	360	0.19	0.26